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Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
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R C van Dijk



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Oxidic composition comprising magnesium, aluminium, and a rare earth metal

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OXIDIC COMPOSITION COMPRISING MAGNESIUM, ALUMINIUM, AND A RARE EARTH METAL

5 The present invention relates to an oxidic composition comprising magnesium, aluminium, and a rare earth metal, the preparation of this oxidic composition, a catalyst composition comprising this oxidic composition, and the use of this oxidic composition for catalytic applications.

10 EP-A 0 554 968 (W.R. Grace and Co.) relates to a composition comprising a coprecipitated ternary oxide comprising 30-50 wt% MgO, 5-30 wt% La₂O₃, and 30-50 wt% Al₂O₃. The composition is used in FCC processes for the passivation of metals (V, Ni) and the control of SO_x emissions.

15 This composition is prepared by precipitating a lanthanum salt, sodium aluminate, and magnesium nitrate with sodium hydroxide from an aqueous solution and aging the precipitate for 10-60 minutes at a pH of about 9.5 and 20-65°C, and filtering, washing and calcining the resulting precipitate at a temperature of 450-732°C.

20 It has now been found that the metal trap capacity of oxidic compositions comprising magnesium, aluminium, and a rare earth metal can be further improved.

This improvement is achieved by increasing the rare earth metal concentration to more than 30 wt%, calculated as oxide and based on total weight of the composition.

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The invention therefore relates to an oxidic composition comprising magnesium, aluminium, and more than 30 wt% of a rare earth metal, calculated as oxide and based on the total weight of the composition.

Examples of suitable rare earth metals are La and Ce.

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The invention further relates to a processes for preparing this oxidic composition, a catalyst composition comprising the oxidic composition, and the use of the oxidic composition in catalytic applications.

- 5 The composition according to the present invention preferably comprises 5 to 60 wt%, more preferably 10 to 40 wt%, and most preferably 20 to 30 wt% Mg, calculated as oxide and based on the total weight of the composition. It preferably comprises 5 to 60 wt%, more preferably 10 to 40 wt%, and most preferably 20 to 30 wt% Al, calculated as oxide and based on the total weight of
10 the composition.

The rare earth metal content in the composition is more than 30 wt%, preferably 35 to 50 wt%, more preferably 40 to 45 wt%, calculated as oxide and based on the total weight of the composition.

15 *Preparation of the composition*

A first method for preparing the oxidic composition according to the invention is a method analogue to EP-A 0 554 968. This method involves precipitation of magnesium, aluminium, and rare earth metal from a solution comprising salts of these metals, followed by calcination of the precipitate.

- 20 The magnesium, aluminium, and rare earth metal can be co-precipitated together, but it is also possible to precipitate the metals in a specific order. For instance, magnesium and aluminium may be co-precipitated to form a first precipitate, after which the rare earth metal is precipitated on this first precipitate. It is also possible to first co-precipitate magnesium and the rare
25 earth metal, followed by precipitation of aluminium on that precipitate, or to co-precipitate aluminium and the rare earth metal, followed by precipitation of magnesium. In between subsequent precipitation steps, the precipitate formed can be aged.

- Suitable salts of these metals are water-soluble salts, e.g. nitrates, chlorides, sulphates, acetates, formates, etc., as the precipitation is preferably conducted
30 from aqueous solution.

In order to precipitate the salts, a base is added to the solution containing the dissolved salts. Any base can be used (such a NaOH, NaHCO₃, NH₄OH, etc.), although it is preferred to use bases that do not contain sodium, as the presence of sodium is known to deteriorate the catalytic performance of many catalyst compositions, especially FCC catalyst compositions.

A second method for preparing these compositions is calcination of a physical mixture of a magnesium source, an aluminium source and a rare earth metal source. The advantage of this method is that it is simple: it requires only a calcination step and does not involve industrially complicated precipitation steps. Further, this method does not require water-soluble salts. Consequently, this method enables the use of a wider spectrum of metal sources and, as it does not necessitate the use of soluble salts, the problems associated with using such salts can be prevented.

The problems associated with using soluble metal salts (e.g. nitrates, chlorides, sulphates) for the formation of an oxidic composition according to the invention include the formation of environmentally harmful gases like NO_x, Cl₂, or SO_x upon calcination. Although these problems can be prevented by filtering and washing the material before calcination, such filtering and washing are industrially complicated and lead to waste water streams containing the anions.

Suitable aluminium sources to be used in this second method include aluminium alkoxide, aluminium oxides and hydroxides such as transition alumina, aluminium trihydrate (gibbsite, bayerite) and its thermally treated forms (including flash-calcined alumina), alumina sols, amorphous alumina, (pseudo)boehmite, aluminium-containing clays such as kaolin, sepiolite, and modified clays such as metakaolin or acid- treated bentonite. Although less preferred, aluminium salts such as aluminium nitrate, aluminium chloride, aluminium chlorohydrate, sodium aluminate, and aluminium sulphate may be used. Mixtures of one or more aluminium sources can also be used.

Suitable magnesium sources to be used in the second method include oxides or hydroxides such as MgO and Mg(OH)₂, hydromagnesite, magnesium carbonate, magnesium hydroxy carbonate, magnesium bicarbonate, and

magnesium-containing clays such as dolomite, saponite, and sepiolite. Although less preferred, magnesium salts such as magnesium acetate, magnesium formate, magnesium hydroxy acetate, magnesium nitrate, and magnesium chloride may also be used. It is also possible to use mixtures of one or more magnesium sources.

Suitable rare earth metal sources to be used in the second method include their oxides, hydroxides, nitrates, chlorides, sulphates, etc. Also bastnaesite can be used as a suitable mixture of rare earth metals.

- 10 The precipitate of the first method - after being isolated from the solution and optionally after washing and filtering - or the physical mixture of the second method, is calcined at a temperature of 200-800°C, more preferably 300-700°C, and most preferably 350-600°C. Calcination is conducted for 0.25-25 hours, preferably 1-8 hours, and most preferably 2-6 hours. All commercial types of
- 15 calciners can be used, such as fixed bed or rotating calciners.

Calcination can be performed in various atmospheres, e.g, in air, oxygen, inert atmosphere (e.g. N₂), steam, or mixtures thereof.

- If desired, the precipitate according to the first method or the physical mixture
- 20 according to the second method may be aged and subsequently dried before performing the calcination step. This aging may be performed in aqueous suspension at either thermal or hydrothermal conditions. Thermal conditions involve temperatures upto 100°C and atmospheric pressure; hydrothermal condition involve temperatures above 100°C and increased pressure, preferably
- 25 autogeneous pressure.

- Further, the precipitate according to the first method or the physical mixture according to the second method may be subjected to a milling step before calcination. In this specification the term 'milling' is defined as any method that
- 30 results in reduction of the particle size. Such a particle size reduction can at the same time result in the formation of reactive surfaces and/or heating of the particles.

The precipitate or physical mixture can be milled in the dry state, or as suspended in a liquid. In the latter case, milling can be performed during the optional aging step. Instruments that can be used for milling include ball mills, high-shear mixers, colloid mixers, and electrical transducers that can introduce
5 ultrasound waves into a slurry. Low-shear mixing, i.e. stirring that is performed essentially to keep the ingredients in suspension, is not regarded as 'milling'.

It is also possible to shape the precipitate of the first method or the physical mixture of the second method to form shaped bodies before calcination.
10 Suitable shaping methods include spray-drying, pelletising, granulating, extruding (optionally combined with kneading), beading, or any other conventional shaping method used in the catalyst and absorbent fields or combinations thereof.

15 If desired, the oxidic composition according to the present invention may contain additives. Examples of such additives are alkaline earth metals (for instance Ca and Ba), transition metals (for example Cr, Mn, Fe, Co, Ti, Zr, Cu, Ni, Zn, Mo, W, V, Sn, Nb), actinides, noble metals such as Pt and Pd, silicon, gallium, titanium, and mixtures thereof.

20 Such additives can be present in amounts of 1 to 20 wt%, preferably 5 to 15 wt%, calculated as oxide and based on the total weight of the composition. Such additives can be incorporated in the oxidic composition by, e.g., impregnation of the oxidic composition with an additive-containing compound, or by having an additive-containing compound present during preparation of the
25 oxidic composition. In the latter case, an additive-containing compound can be added just before or during calcination, it can co-precipitated with the Al, Mg, and/or rare earth metal source during the first method, or it can be physically mixed with the Al, Mg, and/or rare earth metal source during the second method.

Use of the composition

- The oxidic composition according to the present invention is especially suitable for entrapment of metals like Ni and V in FCC processes. For that purpose, the oxidic composition is preferably present in an FCC catalyst or additive. This
- 5 catalyst or additive preferably comprises, apart from the oxidic composition, conventional catalyst ingredients, such as matrix or filler materials (e.g. clay such as kaolin, titanium oxide, zirconia, alumina, silica, silica-alumina, bentonite, etcetera), and/or molecular sieve material (e.g. zeolite Y, ZSM-5, etcetera).
- 10 In addition, use of the oxidic composition in FCC may at the same time result in reduction of SO_x and NO_x emissions and reduction of the sulfur and nitrogen content of fuels like gasoline and diesel.

- Furthermore, the oxidic composition according to the invention can suitably be
- 15 used in or as a catalyst or catalyst additive in a hydrocarbon conversion, purification, or synthesis processes, particularly in the oil refining industry and gas-to-liquid processes. Examples of processes where this composition can suitably be used are hydrogenation, dehydrogenation, hydrocracking, hydroprocessing (hydrodenitrogenation, hydrodesulfurisation,
- 20 hydrodemetallisation), polymerisation, steam reforming, base-catalysed reactions, and Fischer-Tropsch.

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CLAIMS

1. Oxidic composition comprising Mg, Al, and more than 30 wt% of a rare earth metal, calculated as oxide and based on the total weight of the composition.
- 5 2. Process for preparing an oxidic composition according to claim 1, which involves precipitation of a magnesium, an aluminium, and a rare earth metals salt, followed by calcination.
- 10 3. Process for preparing an oxidic composition according to claim 1, which involves the calcination of a physical mixture of a magnesium source, and aluminium source, and a rare earth metal source.
- 15 4. Catalyst composition or catalyst additive composition comprising the oxidic composition according to claim 1.
5. Catalyst composition according to claim 4 comprising a matrix or filler and a molecular sieve.
- 20 6. Use of the oxidic composition of claim 1 or the catalyst composition of claim 4 or 5 in an FCC process.

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ABSTRACT

The invention relates to an oxidic composition comprising Mg, Al, and more than 30 wt% of a rare earth metal, calculated as oxide and based on the total weight of the composition. The invention also relates to a process for preparing such an oxidic composition, which process involves the calcination of a physical mixture of a magnesium source, and aluminium source, and a rare earth metal source.

This composition is suitable as metal trap in FCC processes.

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